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Apparatus for the electrolytic zincing of steel strip

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The invention relates to an apparatus for the zincing of laminated steel strip traversing an electrolytic bath, in which apparatus, by means of contact rollers, the laminated strip constituting the cathode and, in the tank of the bath, anodes arranged opposite the surface of the strip are subjected to the current operating the electrolysis.

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Apparatuses of this kind are used for rendering a steel strip resistant to corrosion by means of zinc coatings; compared with zincing by the passage of strip in a bath of molten zinc; electrolytic zincing has the advantage of supplying a fine layer of zinc uniformly distributed and of virtually constant thickness.

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Use is made for electrolytic zincing more particularly of tanks extending vertically in the main and in which the strip to be zined passes vertically. By means of deflector cylinders, loops may be formed which allow the strip to be introduced into the tank containing the electrolytic bath from the top and also to be removed from it from the top, the number of loops being able to be multiplied, so that it is easy to obtain the residence time required to produce a zinc coating with the desired thickness. It has been found, however, firstly, that the current densities achievable in this way do not make it possible to obtain a coating exhibiting the optimum density and the desirable properties of resistance to wear and, secondly, that the excessively long current paths between the anodes and the strip constituting the cathode require undesirably high electric intensities in order to form the coating. In addition, the consumption of the zinc anodes assumes alarming proportions: due to their retreating surfaces, the already undesirably long current paths become even longer, and the periodical replacement of the anodes that is required leads to very long shut-down periods of the plant. In order to allow for the formation of gas, the height of the tanks is limited. Furthermore, the movement around the deflector cylinders not only increases the resistance to forward movement of the strip, but also produces, in particular if said cylinders have a small radius, permanent deformations, which produce tensions in the strip.

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The aim of the invention is therefore to create an apparatus which makes it possible, with relatively restricted means, to produce dense zinc coatings resistant to wear and having the desired thickness. At the same time the residence time of the strip in the bath, and consequently the length of the path in the bath, have to remain short through the application of strong current intensities. Finally, the apparatus has to ensure a high output while remaining shut down as infrequently and for as short periods as possible.

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To achieve this aim, the invention has devised an apparatus possessing the following characteristics:

- a) a plurality of tanks containing the bath, having a flat and parallelepiped shape, are arranged horizontally and in series, their strip inlet and outlet openings, which are below the level of the baths, being situated more or less on the same level as contact rollers placed, together with the corresponding support rollers, upstream and downstream of said openings,
- b) the surfaces of the top and the bottom of each tank are provided with anodes insoluble in the electrolyte,
- c) the strip outlet openings are equipped with diaphragms which restrict the free width of the latter and with feed tubes directed with a slope from top to bottom and from bottom to top onto the horizontal plane of symmetry, said tubes serving to supply a solution of acid zinc sulfate constituting the electrolyte,
- d) starting from the side walls of the tanks, insulating diaphragms possessing a U-shaped cross-section and directed towards the centre line of said tanks may be displaced by controlled sliding, and
- e) below the tanks and the contact rollers are arranged basins for collecting the electrolyte which flows at the side of the strip inlet, the outlets of said basins being connected to a collector tank connected to a pump for feeding said feed tubes and by a discharge pump to a regeneration plant.

Owing to the use of insoluble anodes, not only is the periodical replacement of the anodes that is required avoided, together with the resulting idle periods, but in addition short distances may be provided between the anodes and the strip, and hence short current paths, which enable the power consumption to be covered with a low intensity.

The separate regeneration of the electrolyte permits the use of simple and inexpensive raw materials for producing the zinc coating. In addition, due to the counterflow supplying of the electrolyte onto the strip, the gas bubbles that form are carried off, which prevents the surface being masked by them.

Other characteristics and advantages of the invention will appear in the detailed description of embodiments given below with reference to the attached drawing. In the latter

- Figure 1 is a view in longitudinal section of a tank containing an electrolytic bath,
- 5 - Figure 2 is a view in cross-section of the tank according to Fig. 1,
- Figure 3 is a plan view of the surface of one of the electrodes according to Figs 1 and 2, and
- Figure 4 shows diagrammatically a plant regenerating the electrolyte.

The longitudinal section reproduced in Fig. 1 represents a flat parallelepiped tank 1 the surface of the top of which is provided with an anode 2, that of the bottom with an anode 3. The anodes each comprise, in order to increase their conductivity, a copper core 4 surrounded on all sides with a lead alloy 5 insoluble in the electrolyte, namely of lead sulfate. The external connection terminals 6 and 7 of the anodes 2 and 3 are also in turn provided with a copper core protected from the electrolyte by a lead alloy jacket. In the faces of the anodes 2 and 3 opposite one another are inserted wear bars 8 of synthetic material which project onto said faces and exclude any contact between the strip 9, which moves horizontally, and the surfaces of the anodes 2 and 3, so that damage and mechanical wear of the anodes are reliably prevented. The tank 1 contains an opening 10 for the entry of the strip which is symmetrical with respect to the plane of symmetry situated between the faces of the anodes 2 and 3 opposite one another. Upstream of said opening 10 are disposed a contact roller 11 and a support roller 12 co-operating with it in order to grip the strip 9. At the other end of the tank 1 is provided an outlet opening 13 downstream of which are disposed a contact roller 14 and a support roller 15 co-operating with it. In the cross-section of the inlet and outlet openings is located a diaphragm 16 or 17, which limits the free section of each of said openings and is of synthetic material, in order not to damage the strip during occasional contact with it, and in order to prevent any short-circuits.

In the area of the outlet opening 13 the tank 1 is equipped with supply tubes 18, which extend in channels directed at an angle onto the strip 9 passing along the plane of symmetry, so that the electrolyte supplied to said tubes runs in the opposite direction to that in which the strip moves forward [through] the gaps formed between the anode 2 and the strip 9 and between the latter and the anode 3. At the other end of the tank the electrolyte exits through the strip inlet opening 10 and flows towards the bottom into a collecting basin 19 situated below the tank 1 and the contact and support rollers 11, 12, 14, 15. The electrolyte collected in said basin is passed, via a drain 20

and a pump 30, into a tank 21 shown in Fig. 4 where it is optionally regenerated before being returned into the supply tubes 18.

In order to construct a strip zincing facility, a plurality of tanks 1 are installed one beside the other, so that the strip, unrolled from a ring gear combined in manner known per se with other ring gears, traverses said tanks one after the other, in a straight line and without changing direction, so that although the residence time in each tank is short, given the length of the latter and the rate of advance of the strip, the sum of said residence times in the tanks 1 ensures the formation of a protective layer of nickel with the desired thickness. Despite the short distances between the anodes and the strip, and hence the small volume of electrolyte in each tank, the subdividing of the residence time prevents both depletion of the electrolyte in zinc and an undesirable enrichment with gas bubbles, which would increase the electrical resistance of the electrolyte, said drawbacks being avoided by the fact that the distance covered by the strip in each tank is relatively short and by the fact that said distance is covered at a relatively high speed.

A cross-sectional view of a tank 1 is illustrated in Fig. 2. Between the anodes 2 and 3 is seen not only the strip 9 but also diaphragms 23 with a U-shaped section and of synthetic material. By means of piston rods 24, said diaphragms 23 may be brought closer to one another by hydraulic jacks 25 and 26 by applying a force to springs 27. Whereas the chamber of the jack 25, namely the chamber situated on the left in the drawing, serves to adjust the position of the corresponding diaphragm and is acted upon by a fluid source under pressure (not shown), the chamber of said same jack that is situated on the right is connected, by a pipe 28, to the one situated to the right of the jack 26. With jacks 25 and 26 of identical diameter, said arrangement ensures that the two diaphragms 23 always move in opposite directions away from one another and at the same distance. The means provided for ensuring the parallelism of the diaphragms 23 have not been shown in the drawing; they may be formed of guide rods or parallel guiding elements, or of other hydraulic jacks arranged parallel with the jacks 25 and 26 and whose synchronism is ensured by a controller or by a cascade arrangement operated by other connecting pipes.

The positioning of the diaphragms 23 is effected preferably in such a way that their flanges 29 include between them an edge zone of predetermined width for a strip 9 passing between said diaphragms. The edges of the strip are thus in the shadow of said flanges 29 of synthetic material, which prevents an excessive current density in the zone of the edges of the strip, and consequently ensures a constant thickness of the zinc layer over the whole width of the strip.

When switching from one strip width to another takes place, the diaphragms may be displaced so that the width of the edge zone masked by their flanges 29 remains the same. Due to the fact that on the two sides the anodes are masked in the zone of the edges of the strip at a distance from the strip, it is ensured that lateral variations in width, an occasional lateral mismatch or other anomaly of this kind do not reach the core of the diaphragms 23, which are therefore shielded from damage.

Fig. 3 is a plan view of the face of the anode 3 turned towards the strip. Said figure shows the position of the wear bars 8 as chevrons offset so as to cover only small parts of the anode. Said parts are distributed regularly over the whole width of the anode in order that the mean current density, measured over the whole width of the anode, remains constant. Said bars are held fast in the anode by dove-tail assemblies. The part of the bars that projects onto the face of the anode is dome-shaped, in order to ensure a weak resistance to the flow of the electrolyte and at the same time not to present steep sides to the leading edge of the strip which is introduced into the tank.

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The operation of the apparatus making use of fixed anodes according to the invention may be rendered automatic and be undertaken by a minimum of personnel and with little maintenance, since it is no longer necessary to replace consumed anodes or to advance wedge-shaped anodes. The zinc to be deposited on the strip is already contained in the electrolyte and is supplied with the electrolyte, which traverses the tank 1, while the gases liberated are evacuated at the outlet of the electrolysis.

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The plant for storage and regeneration of the electrolyte is described below with reference to the diagram of Fig. 4. The electrolyte which exits through the inlet opening 10 of the strip 9 is collected in the collecting basin 19 (Fig. 1) from where it is removed by a pump 30 at the outlet 20. Said pump discharges it into a tank 21 (Fig. 4) fitted with a level detector 31, an apparatus 32 for measuring the pH and an aerometer 33, said three units permitting the volume, the value of the pH and the density of the stored electrolyte to be monitored respectively. Controllers receive the signals of said three units and ensure the observance of tolerances predetermined for said monitored values.

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A zinc sulfate solution having a pH of 1.25 ± 0.2 and a zinc sulfate content of 420 g/litre, with a tolerance of plus or minus 30 g/litre, is used. In order to improve the resistance to wear of the coating of deposited zinc, organic additives are added to the electrolyte, for example 0.1 to 5

g/litre of polyoxyethylene-alkyl amine or polyoxyethylene-alkyl phenol. If the pH value of the electrolyte contained in the tank increases, the apparatus 32 for measuring the pH signals said fact and opens a cock 35 at the outlet of an acid tank 34; an addition of sulphuric acid then causes the pH to drop. If the electrolyte is depleted of zinc sulfate, said fact is signalled by the aerometer 33, which then causes, by means of the pump 36, a removal of enriched solution from the tank 38, via a filter 37, said enriched solution being sent into the collector tank 21. The electrolyte is regenerated in a regeneration container 39 supplied from the tank 21 by means of a pump 40. The electrolyte level in said container or in the tank 38 is measured by means of a detector 41, which, when the level drops, starts up the pump 40. Zinc is introduced into the regeneration container 39 and dissolves in the presence of the excess of sulphuric acid. It has proved to be particularly advantageous not to have to use pure or metallic zinc, contrary to what is the case to order to produce zinc anodes. It suffices, in fact, to introduce into the regeneration container zinc alloys and/or zinc compounds: the sulphuric acid dissolves the zinc contained in said alloys and/or compounds. It is therefore possible to use, for example, the slags produced during hot galvanising, which contain zinc and its oxides, without having to prepare said slags chemically; the use of zinc waste is in turn also possible. Said various possibilities for employing inexpensive materials make it possible to achieve relatively low costs of the process.

By the use of appropriate control devices, the regeneration of the electrolyte and the loss of electrolyte may be operated automatically without difficulty, two main circuits being provided for this purpose. The first circuit is that for the feeding of the tanks 1 with electrolyte. Said feeding is carried out by pumps 22 and is consequently controlled in a specific manner and, if the need arises, may be easily adjusted. In the event of a sudden interruption of the process, it is advantageous to cut off straightaway the inflow of the electrolyte into the tanks 1, in order that the latter, no longer being fed with electrolyte, are drained immediately to avoid damage to the strip. The electrolyte removed from the tanks 1 is caught by collecting basins 19 and returned by pumps 30 into the collector tank 21. A top-up of electrolyte may be provided by an addition of diluted sulphuric acid controlled by means of the cock 35, and also by an addition of water in certain cases. Enrichment with zinc sulfate is effected in a second parallel circuit, in which the electrolyte that requires to be regenerated is passed from the collector tank 21 into the regeneration container 39 by means of the pump 40. After a sufficient stay in said container and the corresponding formation of zinc sulfate, the regenerated solution passes into the tank 38, in which it is clarified. In cases where its density is less than the prescribed value in the collector tank 21, it undergoes an additional cleaning in a filter 37 and is returned into said tank by a pump

36, the electrolyte contained in said tank 21 thus being enriched and in certain cases given a higher density.

It has proved to be important that the circulating pumps 42 are regulated to produce in the tanks 1
5 high rates of flow of the electrolyte, preferably of more than 25 m per minute or even more than 30 m/min.

The embodiments represented in the drawing may be the subject of numerous variants remaining within the scope of the invention. For example, the mechanism for operating the diaphragms 23
10 may be the subject of multiple variations; instead of the hydraulic jacks shown, geared motors whose output gear engages with racks linked to the guide rods of said diaphragms have given good results, as have cams arranged on shafts parallel with the longitudinal axis of the tanks 1, which drive an end face of guide rods whose opposite end bears the diaphragms 23. There may also be the subject of variants the arrangements provided for circulating the electrolyte, as well as
15 those for regenerating the latter, in order to adapt them to the requirements of each case.

In a performance variant, the anodes 2, 3 may be of charcoal. It is also helpful to provide switches for controlling the anodes. In addition, selector switches may be assigned to the tanks in order to connect their anodes (2, 3) to a power source, or to connect the power sources altogether to one of
20 the anodes.

Claims

1. Apparatus for the zincing of laminated steel strip traversing an electrolytic bath, said apparatus, in which the laminated strip constituting the cathode by means of contact rollers and, in the tank of the bath, anodes arranged opposite the surface of the strip are subjected to the current operating the electrolysis, being remarkable in that it exhibits the following characteristics:

a) a plurality of tanks (1) containing the bath, having a flat parallelepiped shape, are arranged horizontally and in series, their inlet (10) and outlet (13) openings for the strip (9), which are below the level of each bath, being situated more or less on the same level as contact rollers (11, 14) placed, together with the corresponding support rollers (12, 15), upstream and downstream of said openings,

b) the surfaces of the top and the bottom of each tank (1) are provided with anodes (2, 3) insoluble in the electrolyte,

c) the outlet (13) openings for the strip (9) are equipped with diaphragms (17) which restrict their free width and with feed tubes (18) directed with a slope from top to bottom and from bottom to top onto the horizontal plane of symmetry, said tubes serving to supply an acid solution of zinc sulfate constituting the electrolyte,

d) starting from the side walls of the tanks (1), insulating diaphragms (23) possessing a U-shaped cross-section and directed towards the centre line of said tanks may be displaced by controlled sliding, and

e) below the tanks (1) and the contact rollers (11, 14) are arranged basins (19) for collecting the electrolyte which flows at the side of the inflow of the strip, the outlets (20) of said basins being connected to a collector tank (21) connected to a pump for feeding said feed tubes (18) and by a pump (40) to a regeneration plant (37, 38, 39).

2. Apparatus according to claim 1, remarkable in that the anodes (2, 3) are of charcoal.

3. Apparatus according to claim 1, remarkable in that the anodes (2, 3) contain a copper core (4) provided with a lead or lead alloy jacket.
4. Apparatus according to any one of the previous claims, remarkable in that the anodes (2, 3) are provided with detachable wear bars (8) of synthetic material.
5. Apparatus according to claim (4), remarkable in that the wear bars (8) are arranged offset on the two sides of the centre plane of the anodes.
6. Apparatus according to any one of the preceding claims, remarkable in that the electrolyte passes at a speed of at least 25 m/min through the space of the tanks (1) that is delimited by the anodes (2, 3).
7. Apparatus according to any one of the preceding claims, remarkable in that the electrolyte passes through the tanks (1) in counter-flow to the strip (9), wherein the sections of the strip inlet (10) and outlet (13) openings provided in the tanks are able to be limited by diaphragms (16, 17).
8. Apparatus according to any one of the preceding claims, remarkable in that the electrolyte is an acid solution of zinc sulfate whose pH varies between 1 and 1.3 and whose concentration varies between 370 and 450 g/litre, wherein there may be added to said solution from 0.1 to 5 g/litre of polyoxyethylene-alkyl amine or polyoxyethylene-alkyl phenol.
9. Apparatus according to any one of the preceding claims, remarkable in that the collector tank (21) is equipped with instruments for measuring (31, 32, 33) the level, the pH and the density of the electrolyte, said instruments controlling cocks or pumps (35, 36) of at least one pipe for topping up with acid or zinc sulfate solution, said cocks or pumps ensuring the supply of acid or solution when prescribed values are not reached.
10. Apparatus according to any one of the preceding claims, remarkable in that at least one regeneration container (39) supplied with zinc or zinc alloys is connected to the collector tank (21), which is able to fill it, the contents of said container being able to be returned into said tank.

11. Apparatus according to any one of the preceding claims, remarkable in that switches may control the anodes (2, 3).
12. Apparatus according to claim 11, remarkable in that it comprises selector switches which are assigned to the tanks (1) in order to connect each of their anodes (2, 3) to a power source, or to connect the power sources altogether to one of the anodes.